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Effect of Temperature and Humidity on Electrical Properties of Organic Orange Dye Complex Films

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Abstract

In this study the effect of temperature and humidity on electrical properties of organic orange dye (OD) complex with vinyl-ethynyl-trimethyl-piperidole (VETP) have been examined. Thin films of OD ($C_{17}H_{17}N_5O_2$) and VETP ($C_{12}H_{19}NO$) complex were deposited from 10 wt.% (5 wt.% of each matter) solution in mixture of distilled water (80%) and spirit. The films were grown at room temperature under normal gravity conditions, *i.e.*, 1 g and in a spin coater at an angular speed of 300 RPM. The Cu/OD-VETP/Cu surface type samples were fabricated and their low frequency (10 Hz) AC electric characteristics were evaluated for the temperature range 30-95°C at ambient humidity of 45-80%. It was observed that at normal conditions the conductivity of the samples is temperature dependent and shows semi-conductive behavior with activation energy of 0.55 eV. It was found that with increase in humidity the resistance of the samples decreases and at humidity values equal to 60-70% the irreversible transition from semi-conductive to conductive state takes place. It is supposed that in the former state the conductive matrix is formed due to incorporation of the water molecules into OD-VETP complex.

Introduction

Characterization of organic materials is important for pure and applied sciences because of their potential use in electronics and instrumentation industry. A lot of industrial applications of organic semiconductors and conductors may be realized by investigating their electrical behavior as a function of doping and device fabrication parameters that influence upon the conductivity of these devices [1-4]. The electrical properties of some of the organic semiconductors, for example proteins, are dependent upon the ambient humidity level and thus it could be potentially used in the development of humidity sensors [1,2]. Whereas, organic semiconductors that show change in their electrical behavior as a function of changed ambient conditions *e.g.*, temperature, radiation and toxic gases are discussed in [5-9]. Inherent ease associated to the fabrication of organic semiconductor devices relative to inorganic one and dependent of their electrical properties on the ambient conditions made them very promising for the development of various type of electronic materials for different kind of application, for example, sensors to evaluate humidity, temperature, light, radiation, strain, *etc*. Over the last years a number of molecular conductors (or metals) on the base of polymers such as polyacetylene (PA) or low molecular tetracyanoquinodimethane (TCNQ) complexes have been synthesized and investigated [3].

The orange dye (OD) is a *p*-type low molecular organic semiconductor and gives good adhesive thin films when applied appropriately at a suitable substrate. In an earlier study [9], we described the electric properties of poly-N-epoxipropylcarbazole (PEPC) and OD heterostructure deposited from solutions and reported that the structure has rectification behavior. In another work [10], the electric properties of the OD films deposited from solution at high gravity were investigated and it was shown that the resistance of the samples does not monotonously on acceleration. The vinyl-ethynyl-trimethyl-piperidole (VETP) is low

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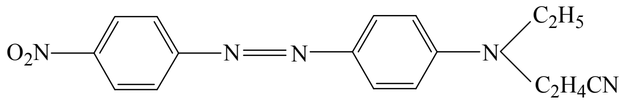
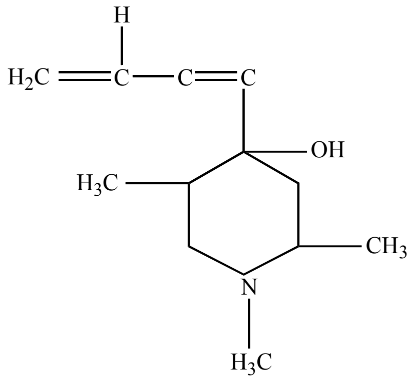
molecular weight organic material too and its electrical properties have not been still investigated. In this paper the effect of temperature and humidity on electric properties of orange dye and vinyl-ethynyl-trimethyl-piperidole complex are reported.

Experimental

In this work commercially available OD and VETP were used for the fabrication of the samples. Figure 1 shows the molecular structures of the OD ($C_{17}H_{17}N_5O_2$) and the VETP ($C_{12}H_{19}NO$). The molecular weights and densities of the OD and VETP were equal to 323 g/mole and 218 g/mole, and 0.9 g/cm^3 and 0.6 g/cm^3 respectively. Red colored thin films of OD and VETP complex were deposited from 10 wt.% (5 wt.% of each matter) solution in mixture of distilled water (80%) and spirit. The films were grown at room temperature under normal gravity conditions, *i.e.*, 1 *g* (during 3-4 hrs) and in a spin coater (during 5-10 min.) at an angular speed of 300 RPM. In the former case the films were observed more uniform. In this work the Cu/OD-VETP/Cu surface type samples (Fig. 2) were fabricated. In this procedure for every sample the volume of used solution was equal to 0.015 ml and the solution was dropped on to the substrate. The average diameter of the OD-VETP complex films on substrates was 5 mm, the gap between copper electrodes was equal to 0.03 mm and the width of organic film "bridge" between electrodes was 5 mm. In different samples the thickness of the OD-VETP films was estimated through optical measurements (in this case the films were deposited on glass substrate) and also by knowing the mass of deposited matter, its density and deposited area. On the average the films thickness was about 0.1 mm. The AC resistance at low frequency (10 Hz) and voltage-current characteristics were measured for the temperature range 30-95°C and at ambient humidity of 45-80% with conventional measurement systems. Temperature and relative humidity were measured with errors of ± 0.5°C and ± 3% respectively. Results obtained on the films deposited at normal gravity conditions (1 g) and in spin coater had some differences in absolute values but electric behavior of the samples coincided in principle.



a) OD



b) VEPT

Fig. 1. Molecular structures of the orange dye (OD) and vinyl-ethynil-trimethyl-piperidole (VETP).

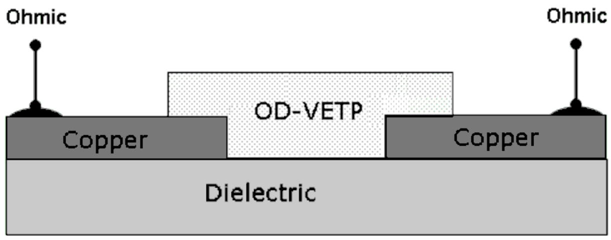


Fig. 2. Crossectional view of a Cu/OD-VETP/Cu surface sample.

Results and Discussion

Figure 3 shows conductivity (σ) versus temperature (T) relationship for the OD-VETP complex, and OD and VETP films as well. Room temperature conductivity of the OD-VETP complex, and OD and VETP films were equal to 6.9×10^{-10} $\Omega^{-1}\times$cm^{-1}, 1.4×10^{-9} $\Omega^{-1}\times$cm^{-1} and 2×10^{-10} $\Omega^{-1}\times$cm^{-1}, respectively. Examination of the figures (Fig. 3) showed that the magnitude of σ increases with the increasing values of temperature. Activation energy (E) was determined from the following well-known expression for the conductivity of organic semiconductors as reported in [1,2]

$$\sigma = \sigma_0 e^{\left(-\frac{E}{kT}\right)} \tag{1}$$

where k is Boltzman constant, T is absolute temperature and σ_0 is pre-exponential factor. Activation energy, that is proportional to the slope of curve in Fig. 3, increases with temperature and for OD-VETP, OD and VETP samples it is in the interval of (0.55-1.58) eV, (0.3-0.95) eV and 0.55-0.62 eV respectively. The observed increase in the activation energy of conductivity as a function of temperature seems to be the activation energy of mobility for hopping related conduction rather than the activation energy for ionic like conduction [11] or electronic excitation energy in semiconductor [12].

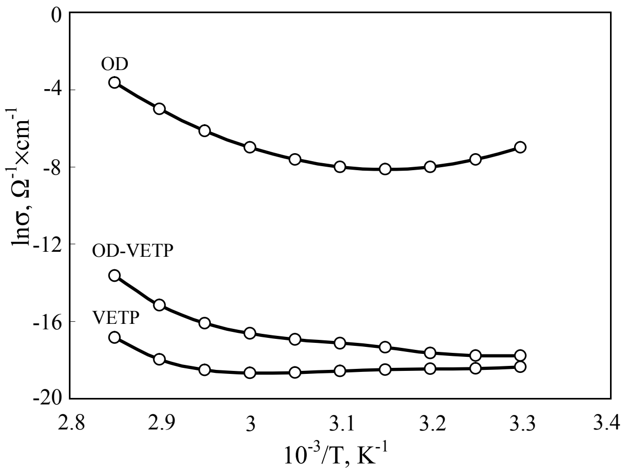


Fig. 3. Dependence of conductivity of OD-VETP, OD and VETP films on temperature.

Figure 4 shows the dependence of the OD-VETP complex films resistance on the humidity level (H, %). Examination of the figures show that the resistance drops with increased level of humidity. Taking R_0 as a reference value observed at lowest humidity, the initial average rate of the drop $d(R/R_o)$ *100%/ dH* is equal to 6.8. The observed sensitivity of the OD-VETP samples to humidity is sufficiently large and this material can be compared from this point with lithium chloride [13,14]. The increase of conductivity of OD-VETP samples with humidity may be due to the ionic and as well as the electronic conduction. In particular, the ionic conduction exponentially depends on dielectric constant of the medium [11]. The absorption of water, which has a relatively high dielectric constant, may enhance the ionic conduction in the OD-VETP films. On the other hand polar molecules of water may increase concentration of holes and thus cause an increase in the electronic conduction in *p*-type semiconductor.

At humidity H = 60-70% the resistance of the samples drops significantly (Fig. 4) that looks like to a transition phenomenon. This transition was irreversible and resistance of the OD-VETP sample remained low at normal humidity and temperature conditions. This state of the OD-VETP sample may be called "conductive" state. Figure 5 shows the dependence of conductivity of the sample on temperature. In the "conductive" state $\sigma = 6.1\ 10^{-5}\ \Omega^{-1}\times cm^{-1}$ and practically it does not depend on temperature analogous to

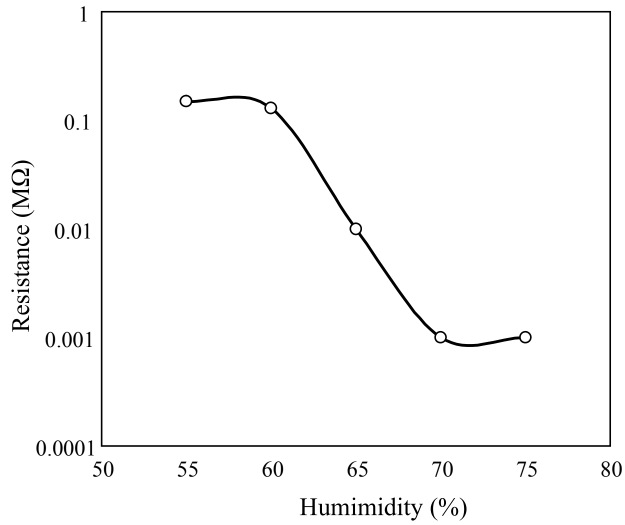


Fig. 4. Dependence of the Cu/OD-VETP/Cu samples resistance on humidity.

some metallic alloys or metals. Though the value of conductivity in the "conductive" state is not in the domain of conventional metals, the temperature dependence of conductivity is like to metallic behavior. It is also confirmed by voltage-current characteristics of the OD-VETP sample (Fig. 6) measured in "conductive" state. On the other hand from voltage-current relationship of the sample in semi-conductive state (Fig. 7) it is seen that resistance of the OD-VETP sample is very large and the characteristics are not linear that confirm the semiconductor behavior of the sample in this state.

Absorption of water molecules by the conductive matter itself can increase ionic [11] and electronic conductance [15] due to their high dielectric constant. But it could explain monotonous and reversible decrease of the OD-VETP resistance on humidity. We suppose that irreversible drop of the resistance on

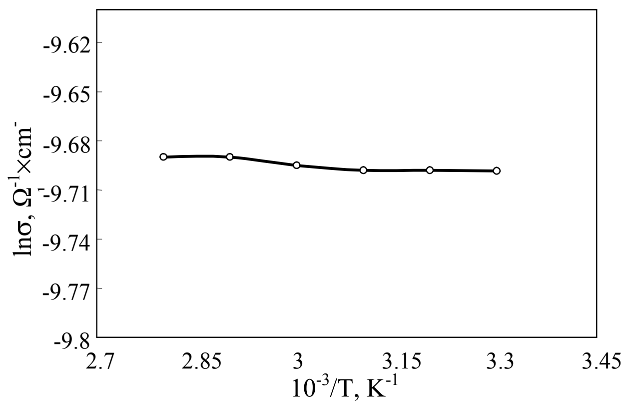


Fig. 5. Temperature dependence of OD-VETP film conductivity in "conductive state".

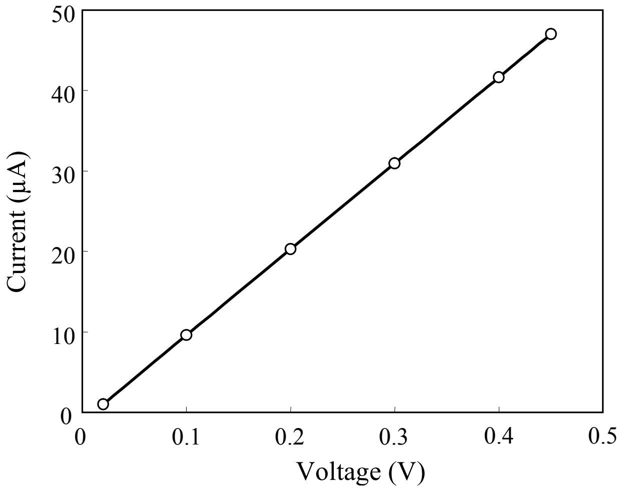


Fig. 6. Voltage-current characteristic of the Cu/OD-VETP/Cu sample in "conductive state".

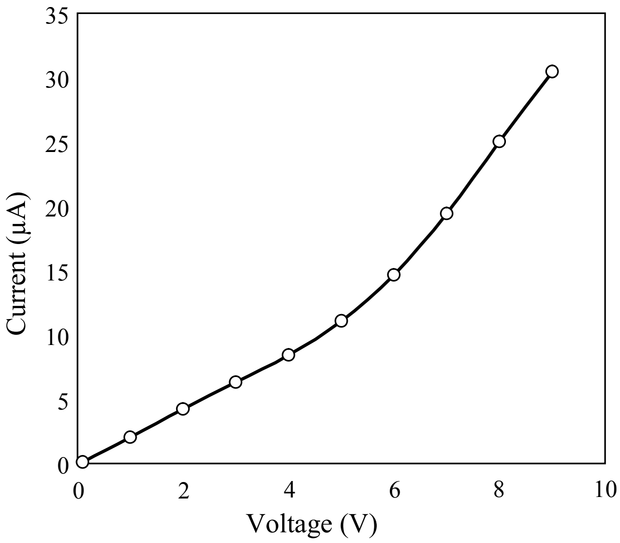


Fig. 7. Voltage-current characteristics of the Cu/OD-VETP/Cu sample in semi-conductive state.

humidity may be due to formation of conductive matrix where water molecules are incorporated into the OD-VETP complex. More detailed investigations are required to make clear the effect of humidity upon conductivity of this complex.

Conclusion

It has been observed that the conduction of orange dye-vinyl-ethynyl-trimethyl-piperidole organic complex films deposited from solution increases with temperature and shows semi-conductive behavior. Examining the effect of humidity on the complex it was observed the irreversible transition from semi-conductive state to "conductive" one. It is supposed that in the former state the conductive matrix is formed due to incorporation of the water molecules into OD-VETP complex.

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